

FORM PTO-132 (REV 10-96)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE	ATTORNEY'S DOCKET NUMBER 13700-0176
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371			U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.52) <b>08/973416</b>
INTERNATIONAL APPLICATION NO. PCT/JP96/01304	INTERNATIONAL FILING DATE May 17, 1996	PRIORITY DATE CLAIMED May 17, 1995	
TITLE OF INVENTION RESIN COMPOSITION AND LAMINATE FOR STORAGE OF LIQUID FOOD			
APPLICANT(S) FOR DO/EO/US HARA, Morio; KOBAYASHI, Norio; TANAKA, Jun; IKENOYA, Tadakatsu; OGITA, Hiroaki			
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:			
<p>1. <input checked="" type="checkbox"/> This is a <b>FIRST</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>2. <input type="checkbox"/> This is a <b>SECOND</b> or <b>SUBSEQUENT</b> submission of items concerning a filing under 35 U.S.C. 371.</p> <p>3. <input checked="" type="checkbox"/> This express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39.</p> <p>4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.</p> <p>5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2))</p> <p>a. <input type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input checked="" type="checkbox"/> has been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US)</p> <p>6. <input checked="" type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)).</p> <p>7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))</p> <p>a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau).</p> <p>b. <input type="checkbox"/> have been transmitted by the International Bureau.</p> <p>c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired.</p> <p>d. <input checked="" type="checkbox"/> have not been made and will not be made.</p> <p>8. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).</p> <p>9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).</p> <p>10. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).</p> <p>Items 11. to 16. below concern document(s) or information included:</p> <p>11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98.</p> <p>12. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.</p> <p>13. <input checked="" type="checkbox"/> A <b>FIRST</b> preliminary amendment. <input type="checkbox"/> A <b>SECOND</b> or <b>SUBSEQUENT</b> preliminary amendment.</p> <p>14. <input type="checkbox"/> A substitute specification.</p> <p>15. <input type="checkbox"/> A change of power of attorney and/or address letter.</p> <p>16. <input checked="" type="checkbox"/> Other items or information: 1. Partial translation of First Written Opinion 2. Partial translation of International Preliminary Examination Report</p>			
EXPRESS MAIL LABEL NO. TB369533626US November 14, 1997			

U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5)		INTERNATIONAL APPLICATION NO. <b>PCT/JP96/01304</b>		ATTORNEY'S DOCKET NUMBER <b>13700-0176</b>	
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17. ☒ The following fees are submitted:

**BASIC NATIONAL FEE (37 CFR 1.492(a)(1)-(5)):**

Search Report has been prepared by the EPO or JPO..... **\$910.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
..... **\$700.00**

No international preliminary examination fee paid to USPTO (37 CFR 1.482)  
but international search fee paid to USPTO (37 CFR 1.445(a)(2)).. **\$770.00**

Neither international preliminary examination fee (37 CFR 1.482) nor  
international search fee (37 CFR 1.445(a)(2)) paid to USPTO..... **\$1040.00**

International preliminary examination fee paid to USPTO (37 CFR 1.482)  
and all claims satisfied provisions of PCT Article 33(2)-(4)..... **\$96.00**

**ENTER APPROPRIATE BASIC FEE AMOUNT =**

Surcharge of **\$130.00** for furnishing the oath or declaration later than ☒ 20 ☒ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE	
Total claims	19 -20 =	0	X \$22.00	\$ --
Independent claims	1 -3 =	0	X \$80.00	\$ --
MULTIPLE DEPENDENT CLAIM(S) (if applicable)				+ \$260.00 \$ --
<b>TOTAL OF ABOVE CALCULATIONS =</b>				<b>\$ 930.00</b>
Reduction by 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28).				\$ --
<b>SUBTOTAL =</b>				<b>\$ 930.00</b>
Processing fee of <b>\$130.00</b> for furnishing the English translation later than <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492(f)).				+ \$ --
<b>TOTAL NATIONAL FEE =</b>				<b>\$ 930.00</b>
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). <b>\$40.00</b> per property				+ \$ 40.00
<b>TOTAL FEES ENCLOSED =</b>				<b>\$ 970.00</b>
				Amount to be: refunded \$ charged \$

**CALCULATIONS PTO USE ONLY**

a. ☒ A check in the amount of \$ 970.00 to cover the above fees is enclosed.

b. ☐ Please charge my Deposit Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_ to cover the above fees.  
A duplicate copy of this sheet is enclosed.

c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 10-1215. A duplicate copy of this sheet is enclosed.

**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO

**Roger T. Frost, Esq.**  
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 191 Peachtree St., N.E., #3700  
 Atlanta, GA 30303

SIGNATURE

Roger T. Frost

NAME

22,176

REGISTRATION NUMBER

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: )  
)  
**MORIO HARA, ET AL.** )  
)  
App. No. \_\_\_\_\_ )  
(National Phase of PCT/JP96/01304 )  
filed May 17, 1996 )  
Filed: **Concurrently Herewith** )  
)  
For: **RESIN COMPOSITION AND LAMINATE** )  
**FOR STORAGE OF LIQUID FOOD** )

**PRELIMINARY AMENDMENT**

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

Please enter the following amendments to the claims of the patent application identified above, before calculating the total amount of filing fee required for that application.

**In the Claims**

Please rewrite the following claims in amended form:

5. (Amended) The resin composition for storing liquid foods of [Claims 3 or 4]

Claim 3, in which the porous inorganic compound comprises synthetic zeolite.

6. (Amended) The resin composition for storing liquid foods of [any one of Claims 1-5] Claim 1, in which the hydrophilic reducing organic compound is a compound selected from the group consisting of ascorbic acids, polyphenols and catechins.

7. (Amended) The resin composition for storing liquid foods of [any one of Claims 1-6] Claim 1, in which the hydrophilic and water insoluble thermoplastic resin is ethylene-vinyl alcohol copolymer, polyvinyl alcohol having a saponification degree of 95% or higher, or polyamide resin.

8. (Amended) The resin composition for storing liquid foods of [any one of Claims 1-7] Claim 1, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

9. (Amended) A laminate for packaging liquid foods comprising an innermost layer made of the resin composition claimed in [any one of Claims 1-8] Claim 1.

10. (Amended) A laminate for packaging liquid foods comprising an innermost layer made of a hydrophilic and water insoluble thermoplastic resin and a layer adjacent to the innermost layer made of the resin composition claimed in [any one of Claims 1-8] Claim 1.

12. (Amended) A laminate for packaging liquid foods comprised of an innermost layer made of resin having a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24\text{ hours}$  at  $40^\circ\text{C}$  and 90% RH and a layer adjacent to the innermost layer made of the resin composition claimed in [any one of Claims 1-8] Claim 1.

17. (Amended) The laminate for packaging liquid foods of [any one of Claims 14-16] Claim 14, in which the porous inorganic compound comprises synthetic zeolite.

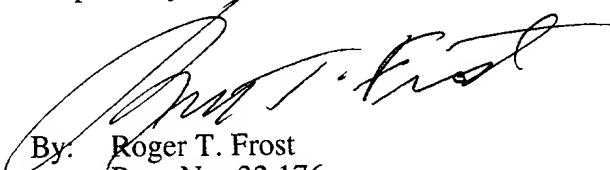
18. (Amended) The laminate for packaging liquid foods of [any of Claims 14-17] Claim 14, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

## REMARKS

These amendments remove multiple dependencies from the claims, thereby reducing the total number of claims for calculating the filing fee. The amended dependencies also place all claims in condition for examination.

The applicants request entry of this amendment and await examination in due course.

Respectfully submitted,

  
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## DESCRIPTION

RESIN COMPOSITION AND LAMINATE FOR STORAGE OF LIQUID  
FOOD.

5

## TECHNICAL FIELD

The present invention relates to a resin composition and a laminate for storage of aqueous liquid food such as juice, milk, liquor and the like.

## BACKGROUND ART

10 Resin containers and paper containers for tightly sealed packaging of liquid food have a wide range of applications because of their adequate strength and lightness.

However, because resin containers and paper containers have a higher oxygen permeability than metal cans, the flavor of the contents of  
15 such containers undergoes degradation, thereby creating a short quality preservation period and other related problems.

Thus, in order to extend quality preservation period, an oxygen barrier resin such as ethylene-vinyl alcohol copolymer or the like is provided in the case of resin containers, and in the case of paper containers,  
20 containers are developed in which a paper base material is laminated by an aluminum foil, an oxygen barrier resin such as ethylene-vinyl alcohol copolymer, polyvinylidene chloride resin or the like, or a resin film on which an inorganic oxide such as silica is deposited. Such containers are used for storage of liquid food.

25 Further, oxygen absorbing containers have been proposed in which an oxidation catalyst such as cobalt stearate or the like, iron powder and a reducing organic compound are included in the resin layer and bonding layer that make up the laminate.

However, in the container laminated by oxygen barrier resin, the  
30 blockage of oxygen is not complete, and in the container laminated by

aluminum foil and resin film on which inorganic oxide is deposited, microscopic cracks (pin-holes) can occur during the lamination and molding process, thereby easily degrading the oxygen gas barrier property.

Further, in the case where iron powder is included, a significant increase in weight is required in order to obtain adequate results, and this makes it impossible to achieve a light-weight container. Moreover, there also exists sanitary problems. In the case where an oxidation catalyst is used, there are problems related to the sanitation and the control of the manifestation of its function.

Moreover, difficulty arises in the case where a reducing organic compound is used because it is necessary to use a safe compound and care must be taken with regards to the heat resistance of the organic compound and the elution from the resin layer.

It is an object of the present invention to provide a resin composition and a laminate which contain a reducing organic compound and which make it possible to safely package and storage liquid food for a long period.

#### DISCLOSURE OF THE INVENTION

Through intensive research, the present inventors were able to complete the present invention by finding that the following resin composition and laminate achieve the object of the present invention. The foregoing resin is obtained by melt kneading a hydrophilic reducing organic compound, or such reducing organic compound and a porous inorganic compound with a hydrophilic and water insoluble thermoplastic resin and then by dispersing the resulted material in a hydrophobic thermoplastic.

The laminate is constructed so that the innermost layer is made of the foregoing composition, or that the innermost layer is made of a specific resin with the layer adjacent thereto being made of the foregoing composition, or that a innermost layer or the layer adjacent to the innermost layer is made of a resin such as polyolefin resin or the like including a porous inorganic compound containing ascorbic acids.

Namely, the gist of the present invention is (1) a resin composition for storing liquid foods, in which a kneaded mixture of a hydrophilic reducing organic compound and a hydrophilic and water insoluble thermoplastic resin is dispersed in a hydrophobic thermoplastic resin; (2) a resin composition for storing liquid foods, in which a kneaded mixture of a hydrophilic reducing organic compound, a porous inorganic compound and a hydrophilic and water insoluble thermoplastic resin is dispersed in a hydrophobic thermoplastic resin; (3) a laminate for packaging liquid foods, having an innermost layer made from the composition described in (1) or (2) above; (4) a laminate having an innermost layer made of a hydrophilic and water insoluble thermoplastic resin and a layer adjacent to the innermost layer made from the composition described in (1) or (2) above; (5) a laminate having an innermost layer made of resin that has a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24 \text{ hours}$  at  $40^\circ\text{C}$  and 90% RH with a layer adjacent to the innermost layer made from the composition described in (1) or (2) above; (6) a laminate having an innermost layer made of a resin layer in which a porous inorganic compound supporting an ascorbic acids is dispersed in a hydrophobic thermoplastic resin; and (7) a laminate having an innermost layer made of resin layer that has a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24 \text{ hours}$  at  $40^\circ\text{C}$  and 90% RH and a layer adjacent to the innermost layer made of a resin in which a porous inorganic compound supporting an ascorbic acids is dispersed in a hydrophobic thermoplastic resin.

In this connection, in the laminate of the present invention, the innermost layer refers to the layer that is closest to the liquid foods, namely the layer that is in direct contact with the liquid foods, when the laminate is used to package liquid foods.

#### BEST MODE FOR CARRYING OUT THE INVENTION

The hydrophilic reducing organic compound in accordance with the present invention may include an ascorbic acids, a polyphenols, a catechins



or the like, and the ascorbic acids may include ascorbic acid, araboascorbic acid or the salts (sodium salt, potassium salt, etc.) thereof and the like.

The polyphenols includes pyrogallol, catechol, gallic acid, resorcin, hydroquinone, and it is possible to use any mixture thereof.

5       The catechins includes epicatechin, epigallocatechin, epicatechin gallate, epigallocatechin gallate, and it is possible to use any mixture thereof.

Among these reducing organic compounds, the ascorbic acids and the catechins are preferred, with ascorbic acid being particularly preferred.

10       With regards to a hydrophilic and water insoluble thermoplastic resin, it is possible to use ethylene-vinyl alcohol copolymer, polyvinyl alcohol having a saponification degree of 95% or higher, polyamide resin (nylon 6, nylon 6.6, nylon 6.12, nylon 11, nylon 12, etc.), polyester resin, acetyl cellulose and the like. Among these, ethylene-vinyl alcohol copolymer is  
15       particularly preferred.

As for a hydrophobic thermoplastic resin, it is possible to use polyolefin resin, polystyrene resin, polyvinyl chloride resin, methacryl resin, ethylene- $\alpha$ -unsaturated carboxylic acid copolymer, ionomer, unsaturated carboxylic acid modified polyolefin, cyclo-olefin copolymer and the like.

20       The polyolefin resin includes polyethylene based resin (low-density polyethylene, medium-density polyethylene, high-density polyethylene, linear low-density polyethylene, etc.), polypropylene based resin (homopolypropylene, ethylene-propylene random copolymer, ethylene-propylene block copolymer, etc.), polybutene-1, polyhexene-1,  
25       polymethylpentene-1 and the like.

The ethylene- $\alpha$ -unsaturated carboxylic acid copolymer includes a copolymer comprised of ethylene and an  $\alpha$ -unsaturated carboxylic acid such as acrylic acid, methacrylic acid or the like.

The unsaturated carboxylic acid modified polyolefin used in the  
30       present invention can be obtained by grafting an unsaturated carboxylic acid

or derivative thereof to the polyolefin resin described above.

The unsaturated carboxylic acid includes  $\alpha$ -unsaturated carboxylic acid,  $\alpha, \beta$ -unsaturated dicarboxylic acid, alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring and the like. Further, the  $\alpha$ -  
5 unsaturated carboxylic acid includes acrylic acid, methacrylic acid, crotonic acid and the like. The  $\alpha, \beta$ -unsaturated dicarboxylic acid or the derivative thereof includes maleic acid, maleic acid anhydride and the like. The alicyclic unsaturated dicarboxylic acid containing a cis-double bond in a ring or the derivative thereof includes HIMIC ACID, HIMIC ACID ANHYDRIDE,  
10 tetrahydrophthalic acid, tetrahydrophthalic acid anhydride, CHLORENDIC ACID and the like.

The cyclic olefin copolymer is a copolymer of cyclic olefin, and ethylene or  $\alpha$ -olefin.

Further, the cyclic olefin includes cyclopentene, cyclohexene,  
15 cycloheptene, cyclooctene, 2-norbornene and the like, and the  $\alpha$ -olefin includes propylene, 1-butene, 1-hexene, 4-methyl-1-pentene and the like.

Among the thermoplastic resins described above, polyolefin resins, and in particular polyethylene based resins and polypropylene based resins are preferred.

20 The porous inorganic compounds used in the present invention includes zeolite, silica gel, sepiolite, porous silica, porous silica-alumina and the like. Among these, zeolite is particularly preferred.

Further, while it is possible to use natural zeolite, synthetic zeolite is preferred in terms of uniformity and purity, with A type, X type and Y type  
25 zeolite being particularly preferred. The synthetic zeolite may be a hydrogen type or cation type (sodium type, potassium type, calcium type, etc.) zeolite.

In this connection, these porous inorganic compounds are preferably dried before being used.

The composition (1) of the present invention is manufactured by dispersing a kneaded compound comprised of the hydrophilic reducing organic compound (hereafter referred to as the A component") and the hydrophilic and water insoluble thermoplastic resin (hereafter referred to as the B component") in a hydrophobic thermoplastic resin (hereafter referred to as the C component"), in which after first kneading the A component and the B component, these components are then kneaded with the C component.

The kneading of the A component and the B component are preferably carried out at a temperature not higher than the melting point or decomposition point of the A component and not lower than the melting temperature of the B component by an appropriate kneading machine, and preferably by an extruder.

Although it is not possible to establish an absolute usage ratio of the A component and the B component because of its dependence on the type of A component and B component, the type of liquid foods, the storage period and the environmental conditions existing inside and outside the storage container, during the kneading of the A component and the B component, the A component should normally be present in the range of 0.1 ~ 50% by weight, and preferably in the range of 0.2 ~ 20% by weight.

Next, the kneaded compound comprised of the A component and the B component obtained as described above is kneaded with and dispersed in the C component to obtain the composition (1) of the present invention. The kneading of the kneaded component and the C component is preferably carried out at a temperature not lower than the melting temperature of the C component in the same manner as the kneading of the A component and B component.

For the same reason as was explained above for the case of kneading the A component and the B component, it is not possible to establish an absolute kneading ratio between the C component and the kneaded compound comprised of the A component and the B component, but in

general in the composition (1) of the present invention the A component should normally be present in the range of 0.05 ~ 10% by weight and preferably in the range of 0.2 ~ 5% by weight, the B component should normally be present in the range of 3 ~ 40% by weight and preferably in the range of 5 ~ 30% by weight, and the C component should preferably be present in the range of 50 ~ 96% by weight and preferably in the range of 65 ~ 95% by weight.

When necessary, it is possible to use a compatibilizer such as maleic acid anhydride modified polyolefin or the like when kneading the C component and the kneaded compound comprised of the A component and the B component. Further, it is also possible to use a sufficiently small amount of well-known antioxidant which does not degrade the hygienic characteristics.

Next, the composition (2) of the present invention is manufactured by dispersing a kneaded compound comprised of the A component, a porous inorganic compound (hereafter referred to as the D component) and the B component in the C component, in which the A component and the D component either simultaneously or separately are kneaded with the B component or after the A component is kneaded with the D component, these components are kneaded with the B component, and then the resultant material is kneaded with the C component. In this connection, it is preferred that after the A component and the D component are mixed together, they be kneaded with the B component, and then the resulted material be kneaded with the C component.

The kneading of the A component, D component and the B component are preferably carried out at a temperature not higher than the melting point or decomposition point of the A component and not lower than the melting temperature of the B component by an appropriate kneading machine, and preferably by an extruder.

Although it is not possible to establish an absolute usage ratio of A

component, D component and B component because it depends on the type of A component, D component and B component, the type of liquid foods, the storage period and the environmental conditions existing inside and outside the storage container, during the kneading of the A component, D component and the B component, the A component should normally be present in the range of 0.1 ~ 50% by weight, and preferably in the range of 0.2 ~ 20% by weight, and the D component should normally be present in the range of 0.1 ~ 30% by weight, and preferably in the range of 0.1 ~ 20% by weight. Further, the ratio of the A component and the D component, D/A (weight ratio), should preferably lie within the range of 0.1 ~ 5.

Next, the kneaded compound comprised of the A component, D component and the B component obtained as described above is kneaded with the C component so that the A component, D component and the B component are dispersed in the C component and the composition (2) of the present invention is obtained. The kneading of the kneaded component and the C component is preferably carried out at a temperature not lower than the melting temperature of the C component in the same manner as the kneading of the A component, D component and B component.

For the same reason as was explained above for the case of kneading the A component, D component and the B component, it is not possible to establish an absolute kneading ratio between the C component and the kneaded compound comprised of the A component, D component and the B component, but in general in the composition (2) of the present invention the A component should normally be present in the range of 0.05 ~ 10% by weight and preferably in the range of 0.2 ~ 5% by weight, the D component should normally be present in the range of 0.05 ~ 10% by weight, and preferably in the range of 0.1 ~ 5% by weight, the B component should normally be present in the range of 3 ~ 40% by weight and preferably in the range of 5 ~ 30% by weight, and the C component should preferably be present in the range of 40 ~ 96% by weight and preferably in the range of 60

~ 95% by weight.

When necessary, it is possible to use a compatibilizer such as maleic acid anhydride modified polyolefin or the like when kneading the C component and the kneaded compound comprised of the A component, D  
5 component and the B component. Further, it is also possible to use a sufficiently small amount of well-known antioxidant which does not degrade hygienic characteristics.

The composition (1) and composition (2) of the present invention obtained as described above can be used as a packaging material for storing  
10 liquid foods; or they can be used while mixing with a raw material for making such a packing material.

Further, the composition (1) and the composition (2) (which may be hereinbelow referred to as the compositions) can be molded into an appropriately shaped molded body which can be used as a liquid foods  
15 container; or the shaped molded body rapped by an appropriate member can be put into a liquid contents.

The present invention includes a laminate for packaging liquid food, in which the innermost layer is made from the foregoing compositions, a laminate in which the innermost layer is made from the hydrophilic and  
20 water insoluble thermoplastic resin with an adjacent layer made from the foregoing compositions, and a laminate in which the innermost layer is made of resin film that has a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24 \text{ hours at } 40^\circ\text{C}$  and 90% RH (relative humidity) and an adjacent layer made from the foregoing compositions. There are no limitations to the  
25 thickness of such laminate, but the thickness may lie within the range  $10 \sim 600 \mu\text{m}$ , which is a normal thickness of a packaging material for storing liquid foods. Of course, it is possible to make the laminate thinner or thicker than this range.

As for the hydrophilic and water insoluble thermoplastic resin used  
30 for the innermost layer, it is possible to select any of the compounds from the

B component which makes up one component of the foregoing compositions, but ethylene-vinyl alcohol copolymer, and polyvinyl alcohol having a saponification degree of 95% or higher are preferred, with ethylene-vinyl alcohol copolymer being particularly preferred.

5           Further, with regards to the resin of the resin layer having the above-described water vapor transmission rate and used for forming the innermost layer, it is possible to use polyolefin resin, polyamide resin, polyester resin, ethylene-vinyl acetate copolymer, ethylene- $\alpha$ -unsaturated carboxylic acid copolymer, ionomer and the like or a combination thereof.

10       From these, polyolefin resin, polyamide resin and ethylene- $\alpha$ -unsaturated carboxylic acid copolymer may be freely selected. Of these, polyolefin resin is preferred, with polyethylene based resin and polypropylene based resin being particularly preferred. Further, even though the thickness of the resin layer which satisfies the above-described water vapor transmission

15       rate depends on such factors as the type of resin and the processing method thereof, it is normally 80  $\mu$  m or less, and in the case of polyethylene based resin and polypropylene based resin, it is normally 30  $\mu$  m or less.

          As for the base material layer of the laminate, it is possible to use any base material normally used in packaging of liquid foods, such as films

20       and sheets made of various synthetic resins, paper, metal foil and the like or a laminate comprised of such materials.

          Further, there is no limitation to the method of laminating the base material layer and the layer comprised of the foregoing composition (which may be hereafter referred to as the resin layer), it is possible to use standard

25       lamination methods.

          For example, it is possible to use a extrusion lamination method in which the resin layer undergoes an extrusion coating onto the base material layer, a dry lamination method in which a film or sheet of the resin layer are laminated onto the base material layer with an adhesive or the like placed

30       therebetween, a direct lamination method in which at least a surface of the

base material layer and the film or sheet resin layer is melted to laminate the two layers together, a so-called sandwich lamination in which the base material layer and the film or sheet resin layer are laminated with an intermediate layer constituting a bonding layer extruded therebetween, and  
5 a coextrusion-lamination method in which a synthetic resin that forms the base material and a resinous kneaded compound that forms the resin layer are extruded from a flat die or circular die provided in an extruder and laminated.

Further, the method of laminating the innermost layer comprised of  
10 the hydrophilic and water insoluble thermoplastic resin and the adjacent layer comprised of the above-described resin layer may be similar to the method of laminating the base material layer and the resin layer. Moreover, the same lamination method is carried out on the innermost layer comprised of the resin layer having the above-described water vapor transmission rate  
15 and the adjacent layer comprised of the above-described resin layer.

In the laminate of the present invention, as described above, the base layer may be made from the base material layer and the above-described resin layer together with the hydrophilic and water insoluble thermoplastic resin or the resin having the above-described water vapor transmission  
20 rate. A layer or layers made of the same material or a different material (e.g., a gas-barrier resin layer, an inorganic compound vapor deposited resin film, etc.) may be provided between the base material layer and the above-described resin or on the outside of the base material layer to construct a multilayered laminate.

25 A container for storing liquid foods formed from the composition (which includes packaging materials, formed material, etc. made therefrom) and the laminate having the above-described construction exhibit an oxygen absorbing function when the water content of the liquid foods filled and sealed inside the container acts on the composition, innermost layer or the  
30 layer adjacent to the innermost layer.



Namely, before filling the contents, the A component is protected by the B component that has an oxygen gas barrier characteristics and is prevented from being consumed by the surrounding oxygen, so that it maintain its oxygen absorbing capability. However, when the contents are filled, the water component gradually reaches through the C component the B component dispersed in the C component, which causes the B component to lose its oxygen barrier characteristics, whereby the A component included therein exhibits an oxygen absorbing function. In particular, when the D component is used together with the A component, the oxygen absorbing function of the A component is improved. Further, when a layer of the resin having the water vapor transmission rate described above is used as the innermost layer, it will improve the sealing characteristics for the contents and reduce the risk of the A component undergoing elusion while maintaining an oxygen absorbing function of the adjacent resin layer.

The present invention further includes a laminate in which the innermost layer is a resin layer manufactured by dispersing a porous inorganic compound supporting ascorbic acids into a hydrophobic thermoplastic resin, and a laminate in which an innermost layer is a resin layer having a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24\text{ hours}$  at  $40^\circ\text{C}$  and 90% RH and a layer adjacent to the inner most layer is a resin layer manufactured by dispersing a porous inorganic compound supporting ascorbic acids into a hydrophobic thermoplastic resin.

The ascorbic acids includes ascorbic acid, araboascorbic acid, the salts thereof (sodium salts, potassium salts, etc.), acyl derivatives (stearoyl and palmitoyl derivatives) and the like.

The porous inorganic compounds can be selected from any of the compounds in the D component, but synthetic zeolite is particularly preferred.

The hydrophobic thermoplastic resin can be selected from any of the compounds from the C component, from which polyolefin resin is preferred,

with polyethylene based resin and polypropylene based resin being particularly preferred.

With regards to the method of making the porous inorganic compound supporting the ascorbic acids, it is possible to employ a method in which both compounds are brought into contact inside an appropriate medium. In this connection, appropriate mediums include alcohols, ethers, ketones, hydrocarbons, halohydrocarbons and the like.

In the preferred method for producing the supporting, the porous inorganic compound is either immersed into a lower alcohol solution, such as an ethanol solution of ascorbic acids, or the solution is passed through a column filled with the porous inorganic compound to cause the solution to be absorbed by the porous inorganic compound. Such methods may also be carried out under heated conditions.

The amount of the ascorbic acids and porous inorganic compound is used in the ratio that the weight of the porous inorganic compound is 1 ~ 50 times larger than that of the ascorbic acids, and in particular in the ratio that the former is 1.2 ~ 10 times larger than that of the latter.

In the method of dispersing the porous inorganic compound that supports an ascorbic acids as described above (that compound is hereinafter referred to a supporting porous inorganic compound) into the hydrophobic thermoplastic resin, it is preferred that both compounds are kneaded at a temperature not lower than the melting temperature of the thermoplastic resin by means of an appropriate kneading machine, preferably an extruder.

Although it is not possible to establish an absolute usage ratio of the supporting porous inorganic compound and thermoplastic resin because it depends on the type of liquid foods, the storage period and the environmental conditions existing inside and outside the storage container, during the kneading of both compounds, the supporting porous inorganic compound should normally be present in the range of 2 ~ 50% by weight, and preferably in the range of 5 ~ 30% by weight.

Because these kneading proportions are used for the resin layer which will form either the innermost layer of the laminate of the present invention or the layer adjacent to the innermost layer, it is possible to prepare in advance a master batch in which the supporting porous inorganic  
5 compound has a ratio that exceeds the above-described ratio, and dilute an appropriate portion thereof with the thermoplastic resin so as to realize the above-described ratio, when forming the laminate.

The laminate of the present invention can be constructed by forming the innermost layer from a resin layer made of the above-described kneaded  
10 compounds. Further, the laminate of the present invention can be constructed from an innermost layer of resin having a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24\text{ hours}$  at  $40^\circ\text{C}$  and 90% RH with an adjacent layer made from the above-described resin. In this connection, there are no limitations to the thickness of such laminated bodies, but the  
15 thickness may lie within the range  $10 \sim 600\ \mu\text{m}$  which is the normal thickness of a packaging material for packaging liquid foods,. Of course, it is possible to make the laminate thinner or thicker than this range.

Further, the resin for resin layer having the above-described water vapor transmission rate for use in forming the innermost layer may be  
20 selected from resin for the resin layer having the water vapor transmission rate previously described above, but of those resins polyolefin resin is preferred, with polyethylene based resin and polypropylene based resin are particularly preferred.

In this connection, the same lamination method as described  
25 previously is used for the base material layer of the laminate and the above-described resin layer. Further, in the laminate of the present invention, the base layer may be made from the base material layer and the above-described resin layer together with the resin layer having the water vapor transmission rate described above. It is possible to provide a layer or layers  
30 made of the same material or a different material between the base material

layer and the above-described resin and on the outside of the base material layer to construct a multilayered laminate.

Further, when the water component of the filled and sealed liquid foods contents acts on the above-described resin layer, the container for  
5 storing liquid foods formed from the laminate of the present invention having the structure described above exhibits an oxygen absorbing function.

Namely, because the ascorbic acids in the resin layer is stable in the presence of oxygen under dry conditions at normal temperatures, it is possible to preserve the above-described function during storage of the  
10 packaging material. However, when filled with contents, the water content passes through the thermoplastic resin and gradually reaches the supporting porous inorganic compound, whereby the ascorbic acid exhibits an oxygen absorbing function.

Further, when the innermost layer is made of a resin layer having a  
15 water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24$  hours at  $40^\circ\text{C}$  and 90% RH, the oxygen absorbing function of the adjacent resin layer is preserved, and at the same time this improves the contents sealing characteristics and reduces the risk of elusion of the ascorbic acids in the resin layer.

## 20 EMBODIMENTS

Next, the present invention will be described by using embodiments.  
(Embodiment 1)

Five parts by weight of ascorbic acid and 95 parts by weight of ethylene-vinyl alcohol copolymer (containing ethylene at 47 molar %, with a  
25 melting temperature of  $160^\circ\text{C}$ ) was supplied to a dual extruder and kneaded, with both substances then being outputted from the die of the extruder in the form of pellet.

Next, 10 parts by weight of the above-described pellet and 90 parts by weight of low-density polyethylene (with a density of  $0.919\text{g/cm}^3$ ) were  
30 kneaded in the same manner as described above to obtain a pellet of the

composition of the present invention having an ascorbic acid content of 0.5% by weight.

Then 50g of this pellet and 10ml of distilled water were placed in a 180ml-volume, oxygen-impermeable, cup-shaped container which was then  
5 sealed by heat sealing with an oxygen-impermeable film.

Next, this container was placed in a constant temperature bath at 15 °C and the concentration of oxygen was measured with an oxygen microanalyzer directly after the heat sealing, after one week and then after two weeks to determine the reduction in the oxygen content, thereby giving  
10 the amounts of oxygen absorbed. These absorbed amounts of oxygen are shown in Table 1.

(Embodiment 2)

Except for using 20 parts by weight of a kneaded compound comprised of ascorbic acid and ethylene-vinyl alcohol copolymer and 80 parts  
15 by weight of low-density polyethylene, the process carried out in this example embodiment was the same as that of Embodiment 1, whereby a pellet of the composition having an ascorbic acid content of 1% by weight was obtained.

Using this pellet, the same oxygen absorbing analysis described in  
20 Embodiment 1 was carried out, and the results thereof are shown in Table 1.  
(Embodiment 3)

Except for using a pellet made of 10 parts by weight of ascorbic acid and 90 parts by weight of ethylene-vinyl alcohol copolymer, the process carried out in this example embodiment was the same as that of  
25 Embodiment 2, whereby a pellet of the composition of the present invention having an ascorbic acid content of 2% by weight was obtained.

Using this pellet, the same oxygen absorbing analysis described in Embodiment 1 was carried out, and the results thereof are shown in Table 1.  
(Embodiment 4)

30 Except for using a compound comprised of 2.5 parts by weight of

ascorbic acid and 2.5 parts by weight of A type zeolite in place of the 5 parts by weight of ascorbic acid, the process carried out in this example embodiment was the same as that of Embodiment 1, whereby a pellet of the composition having an ascorbic acid content of 2.5% by weight and an A type zeolite content of 2.5% by weight was obtained.

Using this pellet, the same oxygen absorbing analysis described in Embodiment 1 was carried out, and the results thereof are shown in Table 1. (Comparative Example 1)

Except for not using ascorbic acid, the process carried out in this comparative example was the same as that of Embodiment 1, and using the thus-obtained pellet, the same oxygen absorbing analysis described in Embodiment 1 was carried out, with the results thereof being shown in Table 1.

(Reference Examples 1 ~ 4)

Except for not using distilled water, the pellets comprised of the compositions of the present invention obtained in Embodiments 1 ~ 4 were subjected to the same sealing, storage and oxygen absorbing analysis as that carried out in Embodiment 1, with the results thereof being shown in Table 1. In this regard, Reference Example 1 corresponds to Embodiment 1, Reference Example 2 corresponds to Embodiment 2, Reference Example 3 corresponds to Embodiment 3, and Reference Example 4 corresponds to Embodiment 4.

**TABLE 1**  
**AMOUNTS OF OXYGEN ABSORBED (ml)**

	Directly after heat sealing	After one week	After two weeks
Embodiment 1	0.0	0.7	1.3
Embodiment 2	0.0	1.1	2.0
Embodiment 3	0.0	2.8	5.2
Embodiment 4	0.0	0.5	1.1
Comparative Example 1	0.0	0.0	0.0
Reference Example 1	0.0	0.0	0.0
Reference Example 2	0.0	0.0	0.0
Reference Example 3	0.0	0.0	0.1
Reference Example 4	0.0	0.0	0.0

5

(Embodiment 5)

A mixture comprised of 10 parts by weight of the pellet made of ascorbic acid and ethylene-vinyl alcohol copolymer obtained in same manner as described in Embodiment 1, 10 parts by weight of maleic acid anhydride  
10 modified linear low-density polyethylene (having a density of 0.91g/cm<sup>3</sup>) and

80 parts by weight of low-density polyethylene (having density of 0.921g/cm<sup>3</sup>) (LDPE) and such LDPE were respectively supplied to an extruder where they underwent a coextrusion by means of a circular die provided in the extruder to form a two-layer inflation film comprised of a 30 μm resin layer  
5 having an ascorbic acid content of 0.5% by weight and a 10 μm LDPE layer.

Next, the two-layer inflation film and a base material comprised of LDPE (15 μm)-paperboard (having basis weight of 200g/m<sup>2</sup>)-LDPE (15 μm)-aluminum foil (7 μm) underwent sandwich lamination at 300°C using a bonding layer of LDPE (having a density of 0.919g/cm<sup>3</sup>) (20 μm) to form a  
10 laminate having the structure described below in accordance with the present invention.

LDPE-paperboard-LDPE-aluminum foil // LDPE // LDPE-ascorbic acid containing resin layer

By using this laminate, a brick-shaped paper container was obtained;  
15 the container was filled with 200ml of deaerated water having a dissolved oxygen concentration of 0.6mg/l by a paper container filling machine so that the ascorbic acid containing resin layer was used for the inside surface of the container.

This container filled with deaerated water was then placed into a  
20 constant temperature bath at 37°C and kept there for a prescribed period of time, during which the concentration of dissolved oxygen in the deaerated water was measured. The results of such measurements are shown in Table 2.

(Embodiment 6)

25 Except for using the pellet obtained in Embodiment 4 in place of the pellet made of ascorbic acid and ethylene-vinyl alcohol copolymer used in Embodiment 5, the laminate constructed in this example embodiment is the same as that of Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table  
30 2.



(Embodiment 7)

In the same manner as was described for Embodiment 5, a three-layer inflation film having the structure described below was formed.

LDPE (10  $\mu$  m)-ascorbic acid containing resin layer (30  $\mu$  m)-LDPE  
5 (10  $\mu$  m)

Except for using this three-layer inflation film in place of the two-layer inflation film described above, the laminate constructed in this example embodiment is the same as that of Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The  
10 results of which are shown in Table 2.

(Embodiment 8)

A three-layer inflation film in which one of the side LDPE layers had 30  $\mu$  m-thickness was formed in the same manner as described above for Embodiment 7. Except for using the 30  $\mu$  m-thick LDPE layer of this three-  
15 layer inflation film for the inside of the container, the laminate is constructed in the same manner as described above for Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table 2.

(Embodiment 9)

20 A three-layer inflation film, in which one of the side layers had a 20  $\mu$  m-thickness and was comprised of a mixture containing 90 parts by weight of polypropylene (having a density of 0.90g/cm<sup>3</sup>) and 10 parts by weight of ethylene-1-butene copolymer (having a density of 0.88g/cm<sup>3</sup>), was formed in the same manner as described above for Embodiment 7. Except for using  
25 the 20  $\mu$  m-thick mixed resin compound layer of this three-layer inflation film for the inside of the container, the laminate is constructed in the same manner as described above for Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table 2.

(Embodiment 10)

A mixture comprised of 10 parts by weight of the pellet made of ascorbic acid and ethylene-vinyl alcohol copolymer obtained in same manner as described in Embodiment 1 and 90 parts by weight of maleic acid anhydride modified linear low-density polyethylene (having a density of 0.91g/cm<sup>3</sup>), and the ethylene-vinyl alcohol copolymer (EVOH) used in Embodiment 1, and the LDPE used in Embodiment 5 were respectively supplied to an extruder, in the same manner as described above in Embodiment 5, where they underwent a coextrusion by means of a circular die provided in the extruder to form a three-layer inflation film having the structure indicated below.

LDPE (10  $\mu$  m)-ascorbic acid containing resin layer (15  $\mu$  m)-EVOH (15  $\mu$  m)

Except for using the EVOH layer of this three-layer inflation film for the inside of the container, the laminate is constructed in the same manner as described above for Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table 2.

(Comparative Example 2)

A three-layer inflation film in which one of the side LDPE layers had a 40  $\mu$  m -thickness was formed in the same manner as described above for Embodiment 7. Except for using the 40  $\mu$  m -thick LDPE layer of this three-layer inflation film for the inside of the container, the laminate is constructed in the same manner as described above for Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table 2.

(Comparative Example 3)

Except for using only ethylene-vinyl alcohol copolymer in place of the pellet made of ascorbic acid and ethylene-vinyl alcohol copolymer, the laminate is constructed in the same manner as described above for

Embodiment 5 and thus underwent the same evaluation as was carried out for Embodiment 5. The results of which are shown in Table 2.

TABLE 2  
CONCENTRATION OF DISSOLVED OXYGEN (mg/l)

Storage Period	Directly after filling	7days	14days	28days
Embodiment 5	0.6	0.6	0.6	0.7
Embodiment 6	0.6	0.6	0.6	0.5
Embodiment 7	0.6	0.6	0.6	0.7
Embodiment 8	0.6	1.0	1.2	1.3
Embodiment 9	0.6	0.7	0.8	0.8
Embodiment 10	0.6	0.7	0.9	1.1
Comparative Example 2	0.6	1.1	1.5	2.3
Comparative Example 3	0.6	1.2	1.6	2.5

(Embodiment 11)

A solution of warm ethanol 7.21 having 300g of ascorbic acid dissolved therein was slowly passed through a glass column filled with 500g of A type zeolite to cause the zeolite to support the ascorbic acid. Then after washing this supporting zeolite with chilled ethanol, drying was carried out at reduced pressure to manufacture ascorbic acid supporting zeolite.

Next, 30 parts by weight of this thus-obtained ascorbic acid supporting zeolite and 70 parts by weight of low-density polyethylene (having a density of  $0.919\text{g/cm}^3$ ) (LDPE) were supplied to a dual extruder and kneaded to obtain a master batch in which the content of the ascorbic acid supporting zeolite is 30% by weight. Then, to lower the ascorbic acid supporting zeolite content to 10% by weight, this master batch and the LDPE used as described above were supplied, together with ethylene-acrylic acid copolymer (having a density of  $0.94\text{g/cm}^3$ ) (EAA), respectively to an extruder to undergo coextrusion from the circular die provided in the extruder to form a two-layer inflation film comprised of a  $30\text{ }\mu\text{m}$  supporting zeolite containing LDPE layer and  $10\text{ }\mu\text{m}$  EAA layer.

Next, this two-layer inflation film and a base material comprised of LDPE ( $15\text{ }\mu\text{m}$ )-paperboard (having basis weight of  $200\text{g/m}^2$ )-LDPE ( $15\text{ }\mu\text{m}$ )-aluminum foil ( $7\text{ }\mu\text{m}$ ) underwent sandwich lamination at  $280^\circ\text{C}$  using a bonding layer of EAA ( $20\text{ }\mu\text{m}$ ) to obtain a laminate of the present invention having the structure indicated below.

LDPE-paperboard-LDPE-aluminum foil // EAA // EAA-supporting zeolite containing LDPE

Using this laminate, a brick-shaped paper container was obtained; the container was filled with  $250\text{ml}$  of deaerated water having a dissolved oxygen concentration of  $0.5\text{mg/l}$  by a paper container filling machine so that the supporting zeolite containing LDPE layer was used for the inside surface of the container.

This container filled with deaerated water was then placed into a constant temperature bath at  $37^\circ\text{C}$  and kept there for a prescribed period of time, during which the concentration of dissolved oxygen in the deaerated water was measured. The results of such measurements are shown in Table 3.

(Embodiment 12)

Using the same process described above in Embodiment 11, a three-layer inflation film was made to have the structure indicated below.

LDPE (10  $\mu$  m)-supporting zeolite containing LDPE (30  $\mu$  m)-LDPE (10  $\mu$  m)

5 Except for using this three-layer inflation film in place of the two-layer inflation film, the laminate is constructed in the same manner as described above for Embodiment 11 and thus underwent the same evaluation as was carried out for Embodiment 11. The results of which are shown in Table 3.

10 (Embodiment 13)

A three-layer inflation film in which one of the side LDPE layers had a 30  $\mu$  m -thickness was formed in the same manner as described above for Embodiment 12. Further, a laminate was constructed in the same manner as was done for Embodiment 11 so that the 30  $\mu$  m -thick LDPE layer of this  
15 three-layer inflation film was used for the inside of the container and thus underwent the same evaluation as was carried out for Embodiment 11. The results of which are shown in Table 3.

(Embodiment 14)

A three-layer inflation film, in which one of the side layers was a 20  
20  $\mu$  m -thick resin mixed layer comprised of a mixture containing 90 parts by weight of polypropylene (having a density of 0.90g/cm<sup>3</sup>) and 10 parts by weight of ethylene-1-butene copolymer (having a density of 0.88g/cm<sup>3</sup>), was formed in the same manner as described above for Embodiment 12.

Further, a laminate was constructed in the same manner as was  
25 done for Embodiment 11 so that the 20  $\mu$  m -thick mixed resin layer of this three-layer inflation film was used for the inside of the container and thus underwent the same evaluation as was carried out for Embodiment 11. The results of which are shown in Table 3.

(Comparative Example 4)

Except for using A type zeolite which does not support ascorbic acid, the laminate was constructed in the same manner as was described for Embodiment 11 and thus underwent the same evaluation as was carried out for Embodiment 11. The results of which are shown in Table 3.

5 (Comparative Example 5)

Except for not using ascorbic acid containing zeolite, the laminate was constructed in the same manner as was described for Embodiment 11 and thus underwent the same evaluation as was carried out for Embodiment 11. The results of which are the same as those of Comparative Example 4.

10

TABLE 3  
CONCENTRATION OF DISSOLVED OXYGEN (mg/l)

Storage Period	Directly after filling	7days	14days	28days
Embodiment 11	0.5	1.1	1.3	1.8
Embodiment 12	0.5	1.2	1.4	1.9
Embodiment 13	0.5	1.3	1.6	2.3
Embodiment 14	0.5	1.2	1.5	2.2
Comparative Example 4	0.5	1.3	2.0	3.1

### INDUSTRIAL APPLICABILITY

15 Because the composition of the present invention exhibits an oxygen absorbing function in the presence of water, when such composition is used for the innermost layer or the layer adjacent to the innermost layer of the laminate of the present invention, or when a container is formed from the

laminate of the present invention which includes a resin layer containing an ascorbic acid derivative, it is possible to absorb not only the oxygen enclosed inside such container, but also oxygen which passes through from the outside of such container, thereby making it possible to reduce the amount of oxygen present. Accordingly, it becomes possible to prevent degradation of the liquid foods due to oxygen during storage, whereby it becomes possible to preserve the quality and extend the shelf life thereof.

Furthermore, it is easy to adjust the oxygen absorbing function by changing the concentration of the reducing organic compound, the kneaded compound mixing proportion of the reducing organic compound and the hydrophilic and water insoluble thermoplastic resin, the concentration of the ascorbic acids supported by the porous inorganic compound, and the amount of supporting porous inorganic compound added. Accordingly, it is simple to carry out adjustments to correspond with the type of foods to be preserved and the internal and external environmental conditions present during storage of such foods.

## CLAIMS

1. A resin composition for storing liquid foods, in which a kneaded compound that includes a hydrophilic reducing organic compound and a hydrophilic and water insoluble thermoplastic resin is dispersed in a hydrophobic thermoplastic resin.
2. The resin composition for storing liquid foods of Claim 1, in which the hydrophilic reducing organic compound is present in the range of 0.05 ~ 10% by weight, the hydrophilic and water insoluble thermoplastic resin is present in the range of 3 ~ 40% by weight, and the hydrophobic thermoplastic resin is present in the range of 50 ~ 96% by weight.
3. A resin composition for storing liquid foods, in which a kneaded compound which includes a hydrophilic reducing organic compound, a porous inorganic compound, and a hydrophilic and water insoluble thermoplastic resin is dispersed in a hydrophobic thermoplastic resin.
4. The resin composition for storing liquid foods of Claim 3, in which the hydrophilic reducing organic compound is present in the range of 0.05 ~ 10% by weight, the porous inorganic compound is present in the range of 0.05 ~ 10% by weight, the hydrophilic and water insoluble thermoplastic resin is present in the range of 3 ~ 40% by weight, and the hydrophobic thermoplastic resin is present in the range of 40 ~ 96% by weight.
5. The resin composition for storing liquid foods of Claims 3 or 4, in which the porous inorganic compound comprises synthetic zeolite.
6. The resin composition for storing liquid foods of any one of Claims 1-5, in which the hydrophilic reducing organic compound is a compound selected



from the group consisting of ascorbic acids, polyphenols and catechins.

7. The resin composition for storing liquid foods of any one of Claims 1-6, in which the hydrophilic and water insoluble thermoplastic resin is ethylene-  
5 vinyl alcohol copolymer, polyvinyl alcohol having a saponification degree of 95% or higher, or polyamide resin.

8. The resin composition for storing liquid foods of any one of Claims 1-7, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

10 9. A laminate for packaging liquid foods comprising an innermost layer made of the resin composition claimed in any one of Claims 1-8.

10. A laminate for packaging liquid foods comprising an innermost layer  
15 made of a hydrophilic and water insoluble thermoplastic resin and a layer adjacent to the innermost layer made of the resin composition claimed in any one of Claims 1-8.

11. The laminate for packaging liquid foods of Claim 10, in which the  
20 hydrophilic and water insoluble thermoplastic resin comprises ethylene-vinyl alcohol copolymer or polyvinyl alcohol having a saponification degree of 95% or higher.

12. A laminate for packaging liquid foods comprised of an innermost layer  
25 made of resin having a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24$  hours at  $40^\circ\text{C}$  and 90% RH and a layer adjacent to the innermost layer made of the resin composition claimed in any one of Claims 1-8.

13. The laminate for packaging liquid foods of Claim 12, in which the resin  
30 layer having the water vapor transmission rate is comprised of polyethylene

based resin or polypropylene based resin having a thickness of  $30\ \mu\text{m}$  or less.

14. A laminate for packaging liquid foods, comprising an innermost layer made of a resin that is prepared by dispersing a porous inorganic compound supporting an ascorbic acids into hydrophobic thermoplastic resin.

15. A laminate for packaging liquid foods comprised of an innermost layer made of a resin having a water vapor transmission rate of not less than  $5\text{g/m}^2 \cdot 24\text{ hours}$  at  $40^\circ\text{C}$  and 90% RH and a layer adjacent to the innermost layer manufactured by dispersing a porous inorganic compound supporting an ascorbic acids into hydrophobic thermoplastic resin.

16. The laminate for packaging liquid foods of Claim 15, in which the resin layer having the water vapor transmission rate is comprised of polyethylene based resin or polypropylene based resin having a thickness of  $30\ \mu\text{m}$  or less.

17. The laminate for packaging liquid foods of any one of Claims 14-16, in which the porous inorganic compound comprises synthetic zeolite.

18. The laminate for packaging liquid foods of any of Claims 14-17, in which the hydrophobic thermoplastic resin comprises polyolefin resin.

19. The laminate for packaging liquid foods of Claim 18, in which the polyolefin resin comprises polyethylene based resin or polypropylene based resin.

## ABSTRACT

The present invention teaches (1) a composition for packaging aqueous liquid foods in which a hydrophilic reducing organic compound or an organic compound and a porous inorganic compound are dispersed in a hydrophobic thermoplastic resin by means of a hydrophilic and water insoluble thermoplastic resin, (2) a laminate for packaging the foods having an innermost layer or a layer adjacent to the innermost layer made of such composition, and (3) a laminate for packaging the foods having an innermost layer or a layer adjacent to the innermost layer made of a hydrophobic thermoplastic resin into which is dispersed a porous inorganic compound supporting an ascorbic acids.

When aqueous liquid foods such as juice, milk or the like are packaged using this composition or laminate, it is possible to prevent degradation due to oxygen existing inside or outside the package, whereby the contents can be safely preserved for a long period of time.

## DECLARATION AND POWER OF ATTORNEY

Attorney's Docket No. 13700-0176

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: RESIN COMPOSITION AND

LAMINATE FOR STORAGE OF LIQUID FOOD

the specification of which

☐ is attached hereto.☐ was filed on \_\_\_\_\_ as application Serial No. \_\_\_\_\_ (if applicable) and was amended on \_\_\_\_\_.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above. I do not know and do not believe that the same was ever known or used by others in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to the date of this application. I further state that the invention was not in public use or on sale in the United States of America more than one year prior to the date of this application. I understand that I have a duty of candor and good faith toward the Patent and Trademark Office, and I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a). I further understand that information is "material" where there is a substantial likelihood that a reasonable patent examiner would consider the information important in deciding whether to allow the application to issue as a patent.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of my foreign application(s) for patent or inventor's certificate listed below, and have also identified below any foreign application for patent or inventor's certificate disclosing subject matter in common with the above-identified specification and having a filing date before that of the application on which priority is claimed:

Country	App. No.	Date of Filing	Priority Claimed Under 35 USC §119
Japan	P7-118426	May 17, 1995	Yes _____ No _____
Japan	P7-118430	May 17, 1995	Yes _____ No _____

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Serial No.	Filing Date	Status: patented, pending, abandoned
PCT/JP96/01304	May 17, 1996	

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patents issuing thereon.

I hereby authorize the U.S. attorneys named herein to accept and follow instructions from **Miyoshi & Miyoshi**, as to any action to be taken in the Patent and Trademark Office regarding this application, without direct communication between the U.S. attorney and the undersigned. In the event of a change in the persons from whom instructions may be taken, the U.S. attorney named herein will be notified by the undersigned.

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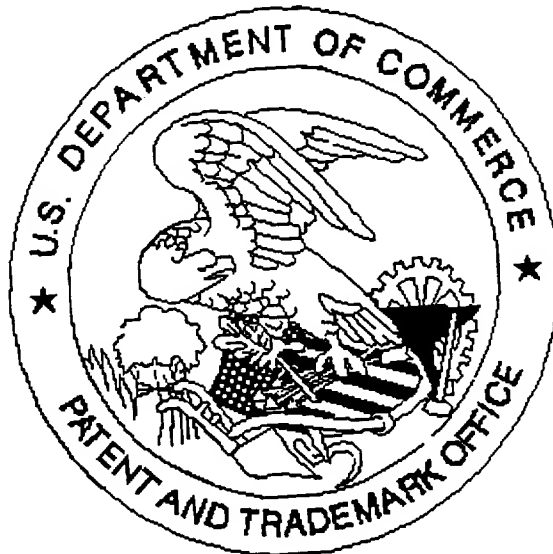
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